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NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Elastomer-coated fabrics

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Wilmington 98,

5 State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and
10 by the following statement:—

This invention relates to elastomer-coated fabrics which are serviceable at elevated temperatures, and more particularly to a fluorinated elastomer coated fabric and a method
15 of making it.

In the manufacture of modern aircraft there is need for a durable sheet material having rubber-like flexibility, good resistance to fuels and lubricants, and extraordinary heat stability. The rapidly expanding guided missile industry is also demanding a rubber-like sheet material which remains strong and flexible during and after use at temperatures up to about 500° F. This material is needed
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for making such items as fuel cells, gaskets and diaphragms, and must therefore have exceptional chemical resistance as well as heat stability.

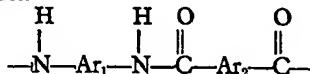
Among known flexible sheet materials, certain elastomer coated fabrics come the closest to satisfying the above-mentioned requirements. But even the best of these are deficient in at least one important property, e.g. heat stability, flexibility, solvent resistance, or chemical resistance. For example, when a heat resistant fabric such as glass fabric is coated with an elastomeric copolymer of vinylidene fluoride and hexafluoropropene, the heat resistance of the product is unsatisfactory, as evidenced by a series loss in tensile and tear strengths when exposed to a temperature of 500° F. for 5 days. When a high quality polyethylene terephthalate fabric is substituted for the glass fabric, the product has even less heat stability. When made
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with a polytetrafluoroethylene fabric, the product is uneconomical and the coating does not adhere well to the fabric; in addition, the high temperature tensile strength is poor.

If coatings of other heat resistant elastomers are applied to glass fabric in attempts to make a suitable product, the coated fabric in each case is inferior to a vinylidene fluoride-hexafluoropropene elastomer coated product in either heat stability or resistance to chemicals and solvents or both. Examples of these other elastomers are silicone rubber, fluorinated silicone rubber, vinylidene fluoride-chlorotrifluoroethylene copolymer and fluorinated butyl acrylate.

The principal object of this invention is to provide an improved elastomer coated fabric characterised by exceptionally high resistance to chemicals, solvents and cracking upon flexing, and resistant to series loss of strength after exposure to temperatures up to about 500° F. for extended periods. Another object is to provide a method for making such a product.

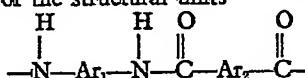
Heat stable coated fabrics according to the present invention comprise an aromatic polyamide fabric having a coating as hereinbefore defined consisting essentially of a cured copolymer containing 30 to 70% by weight of vinylidene fluoride and 70 to 30% by weight of hexafluoropropene, the aromatic polyamide of said fabric being a polymer made up mainly or substantially wholly of the structural units



wherein Ar₁ and Ar₂ are the same or different divalent aromatic radicals in which the chain-extending bonds are attached to non-adjacent carbon atoms in an aromatic ring, and having an inherent viscosity (measured as hereinafter defined) of at least 0.8 and a melting point of at least 300° C. The substituents, if any, are lower alkyl, lower alkoxy,

[Pn]

- halogen, nitro, lower carbalkoxy, or other groups which do not form a polyamide link during the polymerisation. If two or more substituents are present, they may be the same or different. The aromatic polyamides described may be prepared in accordance with the procedure described in the specification of copending Application No. 6636/58 (Serial No. 871,581).
- The invention includes also the method of making a heat stable coated fabric, which comprises coating an aromatic polyamide fabric with a composition consisting essentially of a copolymer containing 30 to 70% by weight of vinylidene fluoride and 70 to 30% by weight of hexafluoropropene and a curing agent, and heating the coated fabric at a temperature of at least 350° F. for a period of time sufficient to cure the said composition, the aromatic polyamide of the fabric being a polymer made up mainly or substantially wholly of the structural units



wherein Ar₁ and Ar₂ are the same or different divalent aromatic radicals in which the chain-extending bonds are attached to non-adjacent carbon atoms in an aromatic ring, and having an inherent viscosity (measured as herein-after defined) of at least 0.8 and a melting point of at least 300° C.

The term "coating", as used throughout the specification and claims, means that the copolymer composition is present within the interstices or on the surface of the fabric or both; the invention thus contemplates impregnated as well as surface coated fabrics.

The inherent viscosity is determined in sulphuric acid (sp. gr. 1.841 at 60° F.) at 30° C. at a concentration of 0.5 gram polymer per 100 cc. of solution. Melting point is determined by conventional procedures such as are described in "The Systematic Identification of Organic Compounds", pages 85—87, by R. L. Shriner and R. E. Fuson (John Wiley and Sons, N.Y., third edition, 1940).

The fabrics which are preferred for use in accordance with the invention are made mainly or wholly from filaments or fibres of poly(*m*-phenylene isophthalamide). Other aromatic polyamides may be used, however, including poly(4-methyl-*m*-phenylene isophthalamide), poly(bis-4-phenylene) methane isophthalamide and poly(*m*-phenylene chloro-isophthalamide). Fibres formed from the reaction product obtained by reacting a solution of bis(4-aminophenyl) sulphone and diethylaniline dissolved in dimethyl tetramethylene sulphone with a solution of isophthaloyl chloride dissolved in dimethyl tetramethylene sulphone, prepared as described in Example XXIV of the specification of copending Application No. 6636/58 (Serial No. 871,581), are also useful in making fabrics to be used in

accordance with the invention. Non-woven fabrics or felts can be used as well as woven and knitted constructions as the substrate for the coating. Other heat resistant fibres or filaments can also be incorporated as a minority component in the fabric structure, such as polytetrafluoroethylene, glass, asbestos and metal fibres. The preferred constructions, however, consist wholly of the heat resistant polyamides.

The copolymers used in making the elastomer coating composition may be prepared by copolymerising about 60 to 15 parts by weight of vinylidene fluoride with about 40 to .85 parts by weight of hexafluoropropene under autogenous pressure at a temperature of about 85 to 100° C., preferably in the presence of a polymerisation initiator. The product of this reaction is an elastomeric copolymer containing about 70 to 30% by weight of vinylidene fluoride units and about 30 to 70% by weight of hexafluoropropene units. These copolymers, and the method of preparing them, are described and claimed in Specification No. 789,786.

The essential components of the coating composition are the above-described copolymer and a curing agent. The latter may be any curing agent capable of bringing about complete cure of the copolymer during a reasonable heating cycle. The proportion of curing agent is not critical. Benzoyl peroxide, dicoumyl peroxide, and hexamethylene diamine carbamate are preferred curing agents.

The coating composition can with advantage contain a curing activator e.g. zinc oxide, dibasic lead phosphate, magnesium oxide, litharge or tribasic lead maleate. It may also contain a filler, e.g. hydrated silica, clay, mica or calcium carbonate, and/or other well known additives, such as release agents, pigments, and plasticisers.

Any desired thickness of coating can be applied to one or both sides of the fabric, employing any suitable method known in the art, e.g. calendering, doctor knife coating, dipping, extruding, or laminating preformed films of the coating composition to the heat resistant fabric by means of heat and pressure.

The coating composition on the fabric may be cured by heating at a temperature of at least 350° F. for a sufficient period of time to render it substantially insoluble when immersed in methyl ethyl ketone at 80° F. for 24 hours. It is preferred to include in the curing operation a brief initial pressing cycle at a temperature of about 320 to 340° F. and a pressure of about 40 to 70 psi.

A surprising advantage of the coated fabrics of this invention over those of the prior art is their exceptional retention of strength and flexibility after prolonged exposure at temperatures up to about 500° F., and even higher. They are even useful for limited

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periods at about 600° F. Another advantage is their retention of these strength properties while at these elevated temperatures. Another particular advantage is their excellent resistance to deterioration and attack by solvents and chemicals which deleteriously affect most of the prior art organic coating compositions. Further advantages are their rubber-like flexibility and flex resistance, and the ease with which they can be made.

There are numerous uses for a material having such a unique combination of properties as the products of this invention. In addition to the previously mentioned uses in the aircraft and guided missile industries, the new materials are useful for making curing

bags for vacuum lamination and conveyor belt-ing.

The following examples illustrate the invention. "Parts" and proportions are by weight.

EXAMPLE I

A heat resistant aromatic polyamide fabric is woven from 160 denier/50 filament yarn made from continuous filaments of a high molecular weight polymer identified as poly(*m*-phenylene isophthalamide). The yarn has a tenacity of 3.9 grams per denier, an elongation value of 45%, and a modulus of 70 grams per denier. Specifications of the fabric are as follows:

	Thickness	- - - - -	5 mils
	Width	- - - - -	14 inches
	Weight	- - - - -	2.6 ozs. per sq. yd.
	Weave	- - - - -	Plain (one over one)
	Thread count	- - - - -	62×61 per inch (warp & weft)
	Tensile strength	- - - - -	27.8 lb. per in. in both directions at 25% elongation (Method 5100*)
40	Tongue tear strength	- - - - -	19.0 lb. in both directions (Method 5134*)

*Methods according to Federal Spec. CCC-T-19 lb., "Textile Test Methods" dated May 15, 1951.

45 A coating composition comprising a fluorinated elastomer is prepared in 3 stages as follows:—

First stage: A so-called "mill mix", formulated as indicated below, is thoroughly blended on a 2-roll rubber mill:—

	Parts
50	Elastomeric reaction product of 50 parts vinylidene fluoride and 50 parts hexafluoropropene - - 250
55	Zinc oxide - - - - - 25
	Dibasic lead phosphite (Dyphos) - 25
	Hydrated silica (Hi-Sil 303) - - 50
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"Hi-Sil" is a Registered Trade Mark.

Second Stage: With a mild agitation, 350 parts of the above blended mill mix are dissolved in 345 parts of methyl ethyl ketone to make 695 parts of solution.

Third Stage: Fifteen parts of benzoyl peroxide dissolved in 90 parts of toluol are mixed with the above solution, making a total of 800 parts of coating composition.

Employing a doctor knife, four coats of the above described elastomeric coating composition are applied to each side of the above described polyamide fabric, with forced drying after each coat to remove most of the volatile components. The coated fabric, about 14 mils thick and substantially dry, is dusted on both sides with "Serecite" mica to minimise surface tack. "Serecite" is a Registered Trade Mark. The coated fabric is press cured for 10 minutes under a pressure of 50

to 60 psi and a platen temperature of 330° F. The pressed and partially cured material is then transferred to an oven, where the temperature is gradually raised over a 2 hour period to 400° F. to allow any residual volatile components to escape without causing blisters in the coating. After the 2 hour period, the coated fabric is heated with an ambient temperature of 400° F. for 24 hours, thus completing the elastomer curing cycle.

The fully cured elastomer coated fabric of this example has a tensile strength of 68×75 lb. per in. (warp×weft), when tested in accordance with Method 5102 of Fed. Spec. CCC-T-19 lb., dated May 15, 1951. After 5 days of exposure to an ambient temperature of 500° F., the tensile strength of the product is substantially unchanged.

The tear strength (trapezoid) of the product of this example is initially 4.8×2.5 lb. (warp×weft) when tested by Method 5136 of Fed. Spec. CCC-T-19 lb., dated May 15, 1951. After the product has been heated for 5 days at an ambient temperature of 500° F., it still has over 75% of its original tear strength.

When a glass fabric is coated in the same manner and with the same composition, the resulting product loses over 50% of its tensile strength and retains only 15 to 30% of its tear strength after being subjected to an ambient temperature of 500° F. for 5 days.

The new coated fabric produced in accordance with this example is thus characterised by a totally unexpected and extraordinary

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degree of heat stability. Even while the product is at the elevated temperature (500° F.), it has good tensile and tear properties.

The rubber-like flexibility and durability of this product are substantially unchanged after 24 hours of immersion at 80° F. in any one of the following solvents and chemicals: gasoline, benzene, diester oil, S.A.E. 20 motor oil, 10% sodium hydroxide and concentrated sulphuric acid.

The product of this example is a particularly useful gasket and diaphragm material for high speed aircraft.

EXAMPLE II

19 A satin-weave aromatic polyamide fabric is made from 290 denier/160 filament yarn, which is constructed of continuous filaments of the high molecular weight aromatic polyamide known as poly(*m*-phenylene isophthalamide). The construction of the fabric is 60×55 (threads per inch in warp and weft).

20 Four coats of the composition described in Example I are applied to the above fabric by alternately dipping it in the elastomer solution and evaporating the solvents. On curing the coated fabric according to the press and oven procedure of Example I, a flexible and durable product is obtained which has the same outstanding heat stability and resistance to solvents and chemicals as the product of that example.

30 The product is useful for making flexible, heat resistant cells for storing guided missile fuels.

EXAMPLE III

The following fluorinated elastomer coating composition is prepared by first mixing the first five ingredients on a rubber mill, and then blending this mixture with the solvents in which the carbamate curing agent has previously been dissolved:—

	Parts
Elastomeric reaction product of	
50 parts vinylidene fluoride and	
50 parts hexafluoropropene	33.74
Zinc oxide	3.71
Carbon black	16.87
Lead stearate	0.34
Hexamethylene diamine carb-	
amate	0.34
Toluol	22.50
Methyl isobutyl ketone	22.50
	100.00

55 Example I is then repeated, except for the substitution of the above described coating composition, with substantially the same results.

EXAMPLE IV

60 The following coating composition is prepared:—

CALENDER COATING COMPOSITION		Parts
Elastomeric reaction product of		
50 parts vinylidene fluoride and		
50 parts hexafluoropropene	100.0	65
Zinc oxide	10.0	
Dibasic lead phosphite	10.0	
Hydrated silica	20.0	
Dicumyl peroxide	3.0	
Stearic acid	0.5	70

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The above ingredients are thoroughly mixed on a water-cooled 2-roll rubber mill.

The aromatic polyamide fabric of Example I is base coated by dipping it in a 40% solution of the above composition (except that the stearic acid is omitted) dissolved in methyl ethyl ketone, followed by forced drying. A total (dry basis) coating weight of 2 oz. per sq. yd. is deposited on both sides of and within the fabric. Then the base coated fabric is calender coated with the above calender coating composition on a three roll calender, whereby a coating weight of 6 oz./sq. yd. is applied to each side of the treated fabric. All three calender rolls are kept at a temperature of 180° F.

The calender coated fabric is cured by the pressing and heating operations used in Example I. When fully cured, the product is useful for making gaskets and diaphragms which retain their desirable properties in the presence of hot aircraft fuels and hydraulic fluids.

EXAMPLE V

95 A high temperature gasket material resistant to corrosive liquids and gases is made by preparing a non-woven batt of poly(*m*-phenylene isophthalamide) 3.0 denier staple fibres 1½ to 3 inches in length on a card. The non-woven batt from the card is needle punched to give it added strength, and is then dipped in the dip coating composition of Example IV, and passed through a heat zone to expel the volatile solvent.

WHAT WE CLAIM IS:—

1. Heat stable coated fabrics comprising an aromatic polyamide fabric having a coating (as hereinbefore defined) consisting essentially of a cured copolymer containing 30 to 70% by weight of vinylidene fluoride and 70 to 30% by weight of hexafluoropropene, the aromatic polyamide of said fabric being a polymer made up mainly or substantially wholly of the structural units



wherein Ar₁ and Ar₂ are the same or different divalent aromatic radicals in which the chain-extending bonds are attached to non-adjacent

- carbon atoms in an aromatic ring, and having an inherent viscosity (measured as hereinbefore defined) of at least 0.8 and a melting point of at least 300° C.
3. Coated fabrics according to Claim 1, in which the aromatic polyamide is poly(*m*-phenylene isophthalamide).
3. Coated fabrics according to Claim 1 or 2, in which the fabric is woven.
10. Coated products according to Claim 1 or 2, in which the fabric is non-woven.
5. Heat stable coated fabrics according to Claim 1 substantially as described in the foregoing examples.
15. The method of making a heat stable coated fabric (as hereinbefore defined), which comprises coating an aromatic polyamide fabric as in Claim 1 with a composition consisting essentially of a copolymer containing 30 to 70% by weight of vinylidene fluoride and 70 to 30% by weight of hexafluoropropene and a curing agent, and heating the coated fabric at a temperature of at least 350° F. for a period of time sufficient to cure the said composition.
25. 7. The method of Claim 6, wherein the curing operation includes a brief initial pressing cycle at 320°—340° F. and a pressure of 40—70 psi.
8. The method of Claim 6 or 7 in which the aromatic polyamide is poly(*m*-phenylene isophthalamide).
9. The method of any of Claims 6 to 8 in which the fabric is woven.
10. The method of any of Claims 6 to 7 in which the fabric is non-woven.
11. The method of making a heat stable fabric according to Claim 6, substantially as described in any of the foregoing examples.

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